Radiochimica Acta 28, 23 – 27 (1981)

Chemical Effects of Isomeric Transition of ^{95m}Tc in Inorganic Tc(IV)-Complexes

By E. IANOVICI, P. LERCH, G. ZAHNER, Institut d'Electrochimie et de Radiochimie, Ecole Polytechnique Federale, Lausanne, Switzerland
and A. G. MADDOCK, University Chemical Laboratory, Cambridge (England)

(Received December 20, 1979; revised July 18, 1980)

Nuclear transformation / Isomeric transitions / Technetium / Hot chemistry

Summary

The chemical effects of the isomeric transition of ^{95m}Tc have been investigated in potassium and ammonium hexachloro-technetate (IV) in solution and solid matrix. The retention of ^{95g}Tc in sulphuric solution was found to be close to zero. Change of the acid concentration had no effect. Nor was 3 M HCl solution much different. The retentions for the solid matrices were found to be higher than 70%. The unretained ^{95g}Tc appeared as cationic, hydrated TcO_2, $[TcCl_5(H_2O)]^-$ and TcO_4^- species. The last species only amounted to about 1%.

1. Introduction

The chemical effects of I.T. of ^{95m}Tc in potassium hexachlorotechnetate adsorbed on an anion exchange resin were observed by BOYD and LARSON [1]. They found that a non negligible proportion of the ^{95g}Tc appeared as $^{95g}TcO_4^-$.
Recently [2] solid ammonium hexachloro-technetate has been shown to have ~70% retention of ^{95g}Tc. The unretained ^{95g}Tc was found as cationic, uncharged and anionic species but practically no $^{95g}TcO_4^-$ was observed. It is possible that the ammonium ion was responsible for these products, so the study of chemical effects of the isomeric transition $^{95m}Tc \rightarrow {}^{95}Tc$ has been extended to potassium hexachloro-technetate in both solution and solid form.
I.T. in solid ammonium and potassium halo-tellurates(IV) [3] and in different oxygenated Te(IV) compounds [3,4] does not lead to any changes in the chemical state of the Te-daughter. In alkaline and acid solutions of the same oxygenated Te(IV) compounds [4] a high retention was also found, about 80% and 95% respectively.

2. Experimental

2.1. Preparation of ^{95m}Tc

The ^{95m}Tc was obtained by the irradiation of natural molybdenum powder with 20 MeV protons in the SIN cyclotron at Villigen, Switzerland. The technetium 95m was separated as TcO_4^- in substantially the same way as previously described [2, 5].

2.2. Preparation of labelled compounds

2.2.1. *Synthesis of* $K_2{}^{99(95m)}TcCl_6$

The $K^{99}TcO_4$ was prepared by the dissolution of $^{99}TcO_2 \times H_2O$ in 3% H_2O_2. The resultant $HTcO_4$ was titrated with 0.1 M KOH and the solution was evaporated to dryness.
The aqueous solution containing $K^{95m}TcO_4$ and the carrier $K^{99}TcO_4$ was evaporated and then dissolved in warm concentrated hydrochloric acid. Powdered potassium iodide was added to reduce the technetium to Tc(IV), [6]. The crystalline potassium hexachloro-technetate(IV) was divided into aliquots for different storage conditions and the samples left for 10 days to reach transient equilibrium.
To study the I.T. in solution the solid $K^{99(95m)}TcCl_6$ was dissolved under red light in 0.1 M, 1 M H_2SO_4 and 3 M HCl. The concentration was 4.2×10^{-2} M. In some experiments hydrogen was bubbled through. To prevent hydrolysis of the $TcCl_6^=$ the samples were kept at 276 K in darkness.

2.2.2. *Synthesis of* $(NH_4)_2{}^{99(95m)}TcCl_6$

A similar labelling method was used to that described previously [2, 7]. Solutions 10^{-3} M and 10^{-4} M were prepared by dissolving the solid product in 1 M H_2SO_4 taking the same precautions as for the K_2TcCl_6 solution. In some experiments hydrogen and nitrogen gas was bubbled through. The samples were kept at 276 K and 293 K in darkness.

2.3. Separation procedure

The separation of the different technetium species was achieved by low voltage electrophoresis. The paper strips used were Schleicher-Schüll No 204013 and the supporting electrolyte was 1 M H_2SO_4 or 1 M HCl. A voltage of 400 V was applied for 2 hours. The dissolution of samples and also the application to the paper strip were made under red light and during operation the electrophoresis apparatus was left in darkness. The temperature was kept at about 280 K. The paper was cut into small pieces before the activity was measured.

2.4. Measurements of the activity

Measurements were made with a high resolution Ge/Li detector connected to an "Ortec" multi-channel analyser. The ^{95g}Tc was measured using the photopeak from 766 keV and the ^{95m}Tc using the photopeak from 835 keV emissions.
The calculation method for the retention and the yield of ^{95g}Tc in the different separated species were described previously [2].

3. Results

3.1. Potassium hexachloro-technetate(IV)

The stability of labelled K_2TcCl_6 with ^{95m}Tc in 1 M H_2SO_4 was checked by measuring the absorption spectra and also by electrophoresis. The absorption spectrum of a sample kept at 276 K in air and in darkness for two weeks gave very nearly the same absorption spectrum as was reported earlier for $TcCl_6^{=}$ ion [8,9]. Nevertheless both electrophoresis and the absorption spectrum show that about 15% of the $^{99}TcCl_6^{=}$ hydrolysed to other species. To see if the hydrolysis of the $TcCl_6^{=}$ ion occurs at the moment of dissolution or later, when the sample is stored experiments with $K_2{}^{99}TcCl_6$ in the absence of ^{95m}Tc were performed. A sample dissolved at room temperature in 1 M H_2SO_4 in darkness showed about the same proportion (10–15%) of hydrolysed $^{99}TcCl_6^{=}$ as for the ^{95m}Tc labelled compound. At 276 K and in darkness the hydrolysis process is extremely slow. These experiments show that no self-radiolysis occurs when the compound is labelled with ^{95m}Tc (not more than 5 μCi).

The hydrolysed $^{99}TcCl_6^{=}$ appears as cationic, uncharged and anionic species. These species were prepared by the hydrolysis of $^{99}TcCl_6^{=}$ in light [10] and separated by electrophoresis. The absorption spectrum of the anionic species was the same as that of $[TcCl_5(H_2O)]^-$ identified by KAWASHIMA *et al.* [11]*. The uncharged species is more likely to be a mixture of hydrated TcO_2 and $[TcCl_4(H_2O)_2]$ species than a pure species [8]. Concerning the nature of the cation it was expected that its spectrum would resemble that reported for $[TcCl_3(H_2O)_3]^+$ [9,10]. Our results showed a shift of the maximum absorption from 350 to 320 nm and in addition an absorption in the visible at 500 nm.
Table 1A presents the distribution of the ^{95g}Tc in sulfuric acid solution of K_2TcCl_6. In 4.2×10^{-2} M K_2TcCl_6 in 1 M H_2SO_4 kept at 276 K, in air and in darkness the retention of ^{95g}Tc is practically zero. The ^{95g}Tc is found as uncharged and cationic species in the preponderant proportion, 76%; about 12% is found as the anion $[TcCl_5(H_2O)]^-$ and about 10% in the higher oxidation state, TcO_4^-. The proportion of the cation was practically the same as the uncharged species. In a few experiments some deviations (< 10%) in the amount of cation were observed due to trailling of the cationic fraction.

Change of sulfuric acid molarity seems to have no important influence on the fate of the ^{95g}Tc. The retention is hardly more than 2% in 0.1 M H_2SO_4 compared to practically zero in 1 M H_2SO_4. The only change concerns $[TcCl_5(H_2O)]^-$ whose yield decreases from 12% to 2%, while an increase is observed for the uncharged species. This is in agreement with the characteristics of the hydrolysis process of the $^{99}TcCl_6^{=}$ ion. In Fig. 1 the proportion of Tc-99, Tc-95m and Tc-95g in the different fractions for K_2TcCl_6 in 1 M sulfuric solution are shown. As expected the yield of ^{99}Tc and ^{95m}Tc in each fraction is the same. The results show only very little the cationic species formed by the aquation of $^{99}TcCl_6^{=}$, but most of the ^{95g}Tc formed by I.T. of ^{95m}Tc appears in this form.

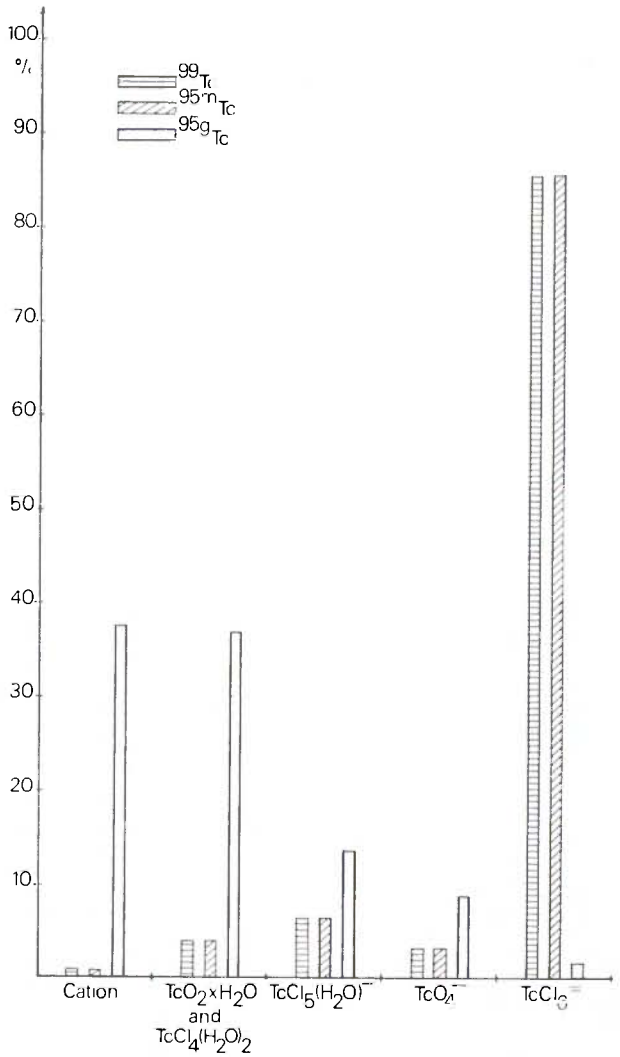

Fig. 1. Distribution of Tc for K_2TcCl_6 in 1 M H_2SO_4 solution. Storage conditions: 276 K, air

* There are at present some discrepancies in the published work on the aquation product from $TcCl_6^{=}$. The species we identify as $[TcCl_5(H_2O)]^-$ has the same spectrophotometric characteristics as the aquation product studied by the Japanese authors [9,10], which agree with earlier data [14] on $TcCl_6^{=}$. But there are no analytical or other data substantiating this formulation. ELDER *et al.* [15] on the other hand provide analytical and crystallographic evidence for $[TcCl_5OH]^=$, but their spectrophotometric data does not agree with anyone else.

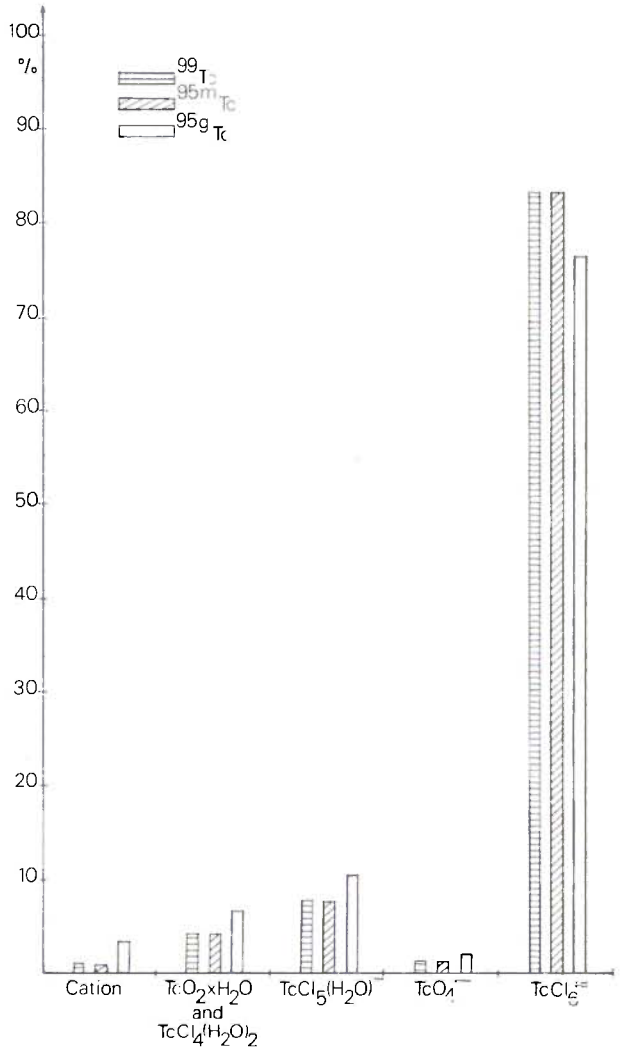

Fig. 2. Distribution of Tc found after dissolution of K_2TcCl_6 in 1 M H_2SO_4. Storage conditions: 293 K, air

The effect of the acid anion was studied by changing to hydrochloric acid. The results for K_2TcCl_6 in 3 M HCl solution are presented in Table IB. The retention is higher under these conditions. The nature of the supporting electrolyte used for the separation has no influence on the retention.

It is interesting to compare the solution results with those for the solid. In Table 2 the results for crystalline K_2TcCl_6 are presented for different conditions of dissolution and storage. The concentration of K_2TcCl_6 upon dissolving was practically the same as for the solution samples. As can be seen the retention is higher than 80%.

The temperature effect is important, the retention decreasing with decreasing temperature. R is about 85% for a sample kept at 276 K under vacuum and 78% for that kept at liquid nitrogen temperature. The decrease of retention is accompanied by an increase in the $^{95g}TcO_4^-$ fraction. In 3 M HCl solution the separation was less efficient.

The distribution of ^{95g}Tc is presented in Fig. 2. As for the solution the ^{95g}Tc appears largely in a positively charged species. A comparison of Figs. 1 and 2 shows that the ^{95m}Tc formed by the hydrolysis of $K_2{}^{99(95m)}TcCl_6^=$ is about the same for the solution kept at 276 K in darkness as for the solid. This result is important because it shows that for solution experiments hydrolysis is not important during the time necessary to reach transient equilibrium. In other words no secondary reactions, due to the hydrolysis, interfere with the stabilization of ^{95g}Tc.

3.2. Ammonium hexachloro-technetate(IV)

The distribution of ^{95g}Tc in 1 M H_2SO_4 solution of $(NH_4)_2TcCl_6$ at different concentrations and different storage conditions are shown in Table 1A. For samples kept at 276 K, independently of the ambient atmosphere and the concentration, the retention is practically zero. At 293 K an acceptable separation of the hydrolysed species was only obtained for solutions saturated with hydrogen. Nevertheless, it seems that the retention at 293 K is hardly higher than at 276 K.

It was observed that for 10^{-4} M solutions kept at 276 K in air the yield of $^{95g}TcO_4^-$ increases at the expence of the cationic and uncharged species. This is suppressed by using a hydrogen saturated solution. It has been found by FERADINI *et al.* [12] that the $TcO_2 \times H_2O$ at a concentration of about 10^{-5} M is easily oxidized to TcO_4^-. For 10^{-3} M solutions the ambient atmosphere becomes unimportant. At 276 K the uncharged species is found in the highest yield followed closely by the cation for both solution and solid.

As noted previously [2] the neutral species, which are formed both by hydrolysis and I.T., are readily oxidized to TcO_4^- by air. But the proportion oxidized decreases rapidly as the chemical concentration of technetium increases. Possibly the aerial oxidation only proceeds rapidly in true solution and becomes negligible when a colloidal $TcO_2 \times H_2O$ phase forms.

Some experiments have been made on the distribution of ^{95g}Tc in deliberately hydrolysed systems. The main new feature seems to be an increase in the proportion of the TcO_4^- fraction.

Further results on I.T. in the $(NH_4)_2TcCl_6$ matrix are presented in Table 2. The solid was dissolved in 1 M H_2SO_4 under the same conditions as for the solution sample. As can be seen the retention is higher than 70% and the unretained ^{95g}Tc is stabilized in cationic, uncharged and anionic species. The proportion of ^{95g}Tc in TcO_4^- ion is about 1%. The storage temperature is more important than the ambient atmosphere. The retention is higher at 80 K than at 293 K, ~82% in comparison with ~71%. The same trend was observed earlier [2] for samples kept in air. The increase occurs at the expense of the cationic and anionic $[TcCl_5(H_2O)]^-$ species. There is no significant difference in the retentions of K_2TcCl_6 and $(NH_4)_2TcCl_6$ kept at liquid nitrogen temperature in vacuum and then dissolved for analysis in 1 M H_2SO_4.

Table 1. *All data means of at least 4 determinations*

Salt used	Concentrations: of salt molar	Concentrations: of acid molar	Conditions: T, K	Conditions: ambient atmosph.	^{95g}Tc distribution: cationic %	uncharged %	$TcCl_5[H_2O]^-$ %	TcO_4^- %	R ($TcCl_6^=$) %
A. Solutions in sulphuric acid									
$K_2^{99(95m)}TcCl_6$	$4.2\cdot10^{-2}$	1	276	air	76.7±2.9		12.7±2.2	9.8±2.2	0.8±0.8
"	"	0.1	276	air	87.0±4.3		2.5±1.5	8.3±1.2	2.1±0.8
$(NH_4)_2^{99(95m)}TcCl_6$	$1\cdot10^{-4}$	1	276	air	11.2±1.7	8.1± 0.5	13.5±1.6	66.7±0.6	0.6±0.9
"	$1\cdot10^{-4}$	1	276	H_2	29.2±2.9	46.4± 1.3	15.0±1.6	9.7±2.0	0.4±0.8
"	$1\cdot10^{-3}$	1	276	air	29.7±1.2	35.5± 3.5	18.1±8.7	16.5±3.8	0.1±0.2
"	$1\cdot10^{-3}$	1	276	N_2	29.8±2.7	41.9± 1.8	12.4±2.8	14.9±3.0	0.9±1.4
"	$1\cdot10^{-3}$	1	276	H_2	30.9±2.8	37.7± 2.8	14.4±3.9	17.0±3.5	0 ±0.1
"	$1\cdot10^{-3}$	1	293	H_2	27.5±5.6	31.4±11.1	16.5±5.0	23.4±5.0	1.6±1.0
"	$1\cdot10^{-3}$	1	293	air		75.3±3.9		18.2±1.0	6.2±1.9
"	$1\cdot10^{-3}$	1	293	N_2		79.0±0.4		14.7±2.5	7.2±2.2
B. Solutions in hydrochloric acid									
$K_2^{99(95m)}TcCl_6$	$4\cdot10^{-2}$	3	276	air	70.2±3.2		12.4±4.9	6.9±2.2	11.4±7.1
"	$4\cdot10^{-2}$	3	276	H_2	71.6±3.6		12.8±3.3	6.0±3.2	9.6±6.2

Table 2. *Chemical distribution of* ^{95g}Tc *formed by* I. T. *in solid matrixes*
Dissolution in 1 M H_2SO_4 and 3 M HCl. All data mean of at least 4 determinations

Salt used	Storage cond.: T, K	Storage cond.: Ambient atmosph.	Unretained ^{95g}Tc: Cation %	$TcO_2\cdot x\,H_2O$ and $TcCl_4(H_2O)_2$ %	$TcCl_5[H_2O]^-$ %	TcO_4^- %	R %
$(NH_4)_2^{99(95m)}TcCl_6$	293	air	8.8 ± 2.0	8.1 ± 0.9	9.2 ± 2.2	0.9 ± 0.6	73.0 ± 3.6
"	293	vacuum	10.8 ± 1.0	7.3 ± 0.2	8.9 ± 1.8	2.0 ± 1.0	71.1 ± 1.4
"	80	vacuum	4.7 ± 0.6	7.0 ± 0.8	5.3 ± 1.6	0.8 ± 0.4	82.1 ± 1.7
$K_2^{99(95m)}TcCl_6$	293	air	7.0 ± 1.1		3.3 ± 0.7	1.5 ± 0.7	88.2 ± 0.6
"	276	vacuum	9.4 ± 1.1		3.0 ± 0.8	2.2 ± 0.5	85.3 ± 1.5
"	80	vacuum	4.6 ± 0.4		1.1 ± 3.1	14.4 ± 2.2	78.8 ± 1.8
*) "	276	vacuum	11.5 ± 2.8		0.5 ± 0.9	6.8 ± 1.9	81.4 ± 3.2

*) Dissolution in 3 M HCl

Discussion

The data for the solid ammonium salt are in substantial agreement with a previous study [2].

It is clear that although there are some quantitative differences in the ^{95g}Tc distributions in the systems using the potassium and the ammonium salts, the retentions in the solid salts are considerable in both cases. For both compounds it is necessary to account for the survival, or reformation on solution for analysis, of more than 70% of the molecular ions that suffer isomeric transitions in their Tc atoms.

This isomeric transition is highly internally converted ($\alpha = 7.6\cdot10^4$ [13]) so that practically every event is followed by an Auger cascade and charging process. This would appear of necessity a localised process unable to involve other atoms directly, irrespective of whether it takes place in a gas or a solid. The maximum kinetic energy of the ejected electrons will be less than 20 keV and in events where more than 2 electrons are ejected some will carry 3 keV or even less energy. There are almost no data on the fate of such electrons in complex polar solids.

In the gas phase there is evidence that charging can lead to molecular rupture by a "Coulombic explosion" [16]. At first it is attractive to suppose that in the solid state such repulsive dissociation, besides being energetically more difficult, has to compete, rather unsuccessfully, with neutralisation by the Auger electrons, the secondaries they have produced and perhaps even by capture from the surrounding lattice. However this only conceals another substantial difficulty. How do the charged technetium atoms dissipate the substantial energy (some tens of eV) released by neutralisation? Can this couple rather efficiently with the phonon spectrum and thus be dissi-

pated to the lattice? Certainly if the observed retentions reflect substantial survival, or virtually immediate reformation, of $TcCl_6^{=}$ there is little room for further rupture of $TcCl_6^{=}$.

It will be noted that the degradation products are very much those expected from mechanical rupture of the $TcCl_6^{=}$. Like the products found following the (n, γ) process in the hexachloro-iridate(IV) salts [17, 18] the principal products seem to arise from ligand stripping of the $TcCl_6^{=}$, without change in oxidation state.

For the solid salts the amount of $^{95g}TcO_4^-$ generally found is very small and it would seem possible that it still reflects some oxidation occurring after solution for analysis.

In solution the Auger electrons and their secondaries are likely to become trapped and solvated. Electron capture from the solvent by the nascent ^{95g}Tc species is likely to lead to a reductive hydrolysis process (as described in [2]) and the very low, or zero, retentions are to be expected.

The main difference in the distribution of separable ^{95g}Tc in the solutions and solids is the generally much higher proportion of pertechnetate in the former systems. This difference can reasonably be attributed to the local production of oxidising species due the radiolytic effect of the Auger electrons. The abnormally high retentions and displacement of the ^{95g}Tc distribution in the direction of less ligand stripping found for hydrochloric acid solutions are not unexpected since one can expect this acid to tend to reverse the aquation and hydrolysis processes.

The fundamental problem posed by these results and by a substantial body of related Mössbauer data, is to give a plausible account of how the excitation arising from low lying vacancies, that initiate Auger cascades, can be dissipated so effectively that very little chemical damage ensues.

Acknowledgements

The authors wish to acknowledge the help of Mr. M. RENAUD in performing the analysis. They are indebted to the team of SIN cyclotron for carrying out the irradiations and for the dosimetric and protection service.

References

1. BOYD, E., LARSON, M. V.: ORNL-2782 (1959).
2. IANOVICI, E., LERCH, P., PROSO, Z., DECOMBAZ, M., MADDOCK, A. G.: Radiochim. Acta **26**, 141 (1979).
3. AMBE, S., SAITO, N.: Radioisotopes **21**, 17 (1972).
4. ZAITSEV, V. M., GUSEL'NIKOV, V. S., MAKHOMALKINA, S. M.: Radiokhimia **14**, 783 (1972).
5. KOTIGOV, K. V., RAVKOV, O. M., SHVEDOV, V. P.: Technetium, in: *Advances in Inorg. Chem. and Radiochem.*, vol. 11, Ed. H. J. EMELEUS and A. G. SHARP, Academic Press, London 1968.
6. DALZIEL, J., GIEL, N., NYHREM, R. S., PEACOCK, R. D.: J. Chem. Soc. 4012 (1958).
7. SHUKLA, S. K.: Ric. Sci. **36**, 1202 (1966).
8. KANCHIKU, Y.: Bull. Chem. Soc. Japan **42**, 2831 (1969).
9. KOYAMA, M., KANCHIKU, Y., FUJINAGA, T.: Coord. Chem. Rev. **3**, 285 (1968).
10. IANOVICI, E., LERCH, P., KOSINSKI, M.: to be published.
11. KAWASHIMA, M., KOYAMA, M., FUJINAGA, T.: J. Inorg. Nucl. Chem. **38**, 819 (1976).
12. FERADINI, C., CARLIER, R., GENET, M., PUCHEAUT, J.: Radiochim. Acta **12**, 1 (1969).
13. HAGER, R. S., SELTZER, E. C.: Nuclear Data A4, 1 (1968).
14. JØRGENSEN, C. K., SCHWOCHAU, K.: Z. Naturforsch. **20a**, 65 (1965).
15. ELDER, M., FERGUSSON, J. E., GAINSFORD, G. J., HICKFORD, J. H., PENFOLD, B. R.: J. C. S. A, 1423 (1967).
16. CARLSON, T. A., WHITE, R. M.: J. Chem. Phys. **48**, 5191 (1968).
17. CABRAL, J. M. P., MADDOCK, A. G.: J. Inorg. Nucl. Chem., and refs. therein, **29**, 1825 (1967).
18. VAN OOIJ, W. J., HOUTMAN, J. P. W.: Radiochim. Acta **21**, 136, 142, and refs. therein, (1974).